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Electronic transitions and excitations in solid C_{70} studied by EELS and XPS C 1s satellite structures

Bo-ying Han, Li-ming Yu, K. Hevesi, G. Gensterblum, P. Rudolf, J.-J. Pireaux, P. A. Thiry, R. Caudano, Ph. Lambin, and A. A. Lucas

Institute for Studies in Interface Sciences, Facultés Universitaires Notre-Dame de la Paix, 61 rue de Bruxelles, B-5000 Namur, Belgium

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The electronic transition and excitation properties of highly ordered C_{70} films have been studied by reflection electron-energy-loss spectroscopy (EELS) and x-ray photoemission spectroscopy (XPS) C 1s satellite structures. The EELS study revealed a total of 11 features in the energy-loss range 1–40 eV. These include two tight-binding Frenkel excitonic levels in C_{70} fullerite, at 1.53 and 1.88 eV; the feature at 2.20 eV correlated with the onset of the electron transitions between the highest occupied molecular-orbital- and lowest occupied molecular-orbital-derived bands; a doublet at around 6 eV showing evidence of the π-plasmon splitting of fullerite C_{70}. A broad hump at $\sim$28 eV corresponds to the excitation of the $(\sigma+\pi)$ plasmon. The XPS C 1s satellite structures were found to be in overall agreement with the EELS results in the corresponding energy-loss range. By comparing the EELS data with the direct and inverse photoemission data, the on-site Coulomb correlation energy has been determined to be 1.2±0.2 eV for C_{70} fullerite.

I. INTRODUCTION

C_{70} is the second most stable and abundant fullerene, just next to C_{60}. Molecular C_{70} has an ellipsoidal structure with D_{5h} symmetry.[1–4] At room temperature, solid C_{70} mainly adopts one of the close-packed structures, namely face-centered cubic (fcc) or hexagonal close packed (hcp), depending on the history of its formation.[5–10] Various experimental methods have been used to explore the electronic and structural properties of C_{70}: visible-ultraviolet optical absorption spectroscopy for C_{70} in solutions[3,11] and for solid C_{70} films,[12] photoluminescence for C_{70} in solutions[13] and as solid films,[14] photoemission and inverse photoemission,[15–17] x-ray diffraction,[5–7] electron microscopy,[5,9] electron-energy-loss spectroscopy operating in the transmission mode (T-EELS),[18,19] and in the reflection mode (R-EELS),[20] x-ray absorption spectroscopy (XAS),[21] etc. Meanwhile, a number of theoretical calculations have been carried out on the electronic and crystalline structure of C_{70} fullerite.[22–28] Nevertheless, our present state of knowledge about C_{70} is not as well advanced as for C_{60}. The lower molecular symmetry and the more complex crystal structure of C_{70} complicate the determination of its molecular orbitals and its energy band structure in the condensed phase. Due to its elongated molecular shape, experimental difficulties have been encountered in preparing high-quality ordered C_{70} fullerite samples, which are necessary for an accurate and unambiguous characterization of its solid-state properties. To our knowledge, only one publication up to now has reported the growth of highly ordered "thick" (>100 Å) C_{70} films.[29] Further theoretical and experimental efforts are still required to get a more comprehensive understanding of C_{70} fullerite.

In this paper, we report on a combined reflection electron-energy-loss spectroscopy and x-ray photoelectron spectroscopy (XPS) (C 1s satellite line structure) study of highly ordered C_{70} films. From the experimental point of view, with its excellent energy resolution (≤ 0.06 eV) and high sensitivity attainable by the strong interaction of low-energy incident electrons (typical kinetic energy 5–100 eV), R-EELS is at its best for measuring the electronic transitions and excitations in the relevant energy range (near infrared, visible, and ultraviolet). In the only previous report of the R-EELS study on pure polycrystalline C_{70} fullerite,[20] it was stated that due to instrumental limitations the experiment was conducted at much lower energy resolution (0.8 eV). Indeed, apart from the two collective valence-electron excitations (plasmons) reported in Ref. 20, we have identified a number of other weak loss peaks.

The XPS core-line satellite structure also provides information on the electronic transitions and excitations of a system. While EELS generally probes the excited states of the neutral system, XPS core-line satellite structures give information both on the ionized molecule, through on-site interaction, and on the neutral molecular lattice, by the inelastic losses that the photoelectron experiences when it propagates through the lattice (through off-site processes). The second mechanism resembles that occurring in EELS. An improved XPS setup[30] (with high-intensity, monochromatized x rays, and high-resolution photoelectron energy analyzer) enables us to get an additional perspective on the electronic excitations and transitions of the system under investigation.

These two methods are to some extent complementary. As already mentioned, EELS generally provides insight into the electronic states of the neutral molecules and lattice; whereas XPS satellite structure carries information on both the ionized molecule from which the photoelectron originates and the neutral molecular lattice. Since an ionized molecule often possesses a different geometrical symmetry compared to a neutral molecule of the same

species, the selection rules governing the electronic transitions are expected to work differently. Hence, a more comprehensive picture of the electronic states of a system can be obtained by comparing the experimental results from these two methods. A proper combination of these two methods is a powerful way for probing the electronic transitions and excitations of solids.

EELS spectra of C_{70} fullerite reveal a total of 11 features in the energy-loss range 1–40 eV. These include the excitation of two molecular excitonic levels in C_{70} fullerite, at 1.53 and 1.88 eV; the feature at 2.20 eV correlated with the onset of the electron transitions between the energy bands derived from the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the C_{70} molecule; the prominent peak at $\sim$2.55 eV revealing the first dipole-allowed electron transition in C_{70} fullerite; and a doublet at $\sim$5.2 and $\sim$5.9 eV which probably corresponds to the two split levels of the π plasmon of C_{70} induced by its ellipsoidal molecular shape. A broad hump at $\sim$28 eV corresponds to the excitation of the $(\sigma+\pi)$ plasmon. Some of these features, including two peaks at 2.55 and 3.2 eV as well as two plasmon peaks, had previously been observed in T-EELS of a solid C_{70} film (prepared directly from a C_{70} toluene solution),[18] yet no discussion about the peaks originating from individual electronic transitions had been provided.

The XPS C 1*s* satellite structures of C_{70} fullerite have been found in overall agreement with the EEL spectra in the corresponding energy-loss range, notwithstanding significant peak intensity modulations. A few weak features, undetected in EEL spectra, have been identified. Our high-resolution data are in agreement with the recently published C 1*s* satellite structures of C_{70} fullerite.[17]

Throughout this paper, we endeavor to compare, whenever possible, our results with those obtained with other techniques, particularly near-infrared and visible optical absorption spectroscopy,[3,11,12] photoluminescence spectroscopy,[13,14] x-ray absorption spectroscopy,[21] and transmission electron-energy-loss spectroscopy.[18]

II. EXPERIMENTAL DETAILS

The EELS experiments were performed in a two-chamber ultrahigh-vacuum (UHV) system equipped with a high-resolution spectrometer (ISA-Riber).[31] The base pressure in the analysis and preparation chambers was 6×10^{-11} and 3×10^{-10} mbar, respectively. The spectrometer consists of two identical hemispherical electrostatic selectors, one acting as monochromator, the other as analyzer. The energy of the incident electron beam can be varied from 0 up to 150 eV. For the study of electronic transitions and excitations, the instrumental resolution is set to 0.03–0.06 eV. The spectrometer has an acceptance angle of 1.5°. All the EELS measurements presented in this paper were carried out in the specular reflection geometry ($\theta_i=\theta_r=45°$, or $\theta_i=\theta_r=60°$).

The XPS spectra were recorded with a SCIENTA ESCA-300 spectrometer using monochromatized Al $K\alpha$ x rays from a rotating anode, and a high-resolution photoelectron energy analyzer.[30] A high instrumental resolution (0.3 eV) was achieved. The base pressure of the XPS analysis and preparation chambers was, respectively, 2×10^{-10} and 5×10^{-10} mbar.

Purified C_{70} powder ($\geq$98%) was obtained from a commercial source (MER Corp., Tucson, AZ). C_{70} was sublimed at $\sim$450 °C from a Knudsen cell, which had been previously carefully outgassed up to $\sim$500 °C. Two lamellar materials, MoS_2 and GeS, were used as substrates. They were cleaved in vacuum (using an adhesive tape), along the surfaces (0001) for MoS_2 and (001) for GeS. The substrate was heated from the back side by a tungsten filament to $\sim$150 °C during C_{70} deposition. The evaporation rate was monitored by a quartz crystal oscillator and its typical value as 1–3 Å/min. Highly ordered C_{70} films were obtained on both substrates, as evidenced by sharp low-energy electron diffraction (LEED) patterns characteristic of the close-packed C_{70} molecular arrangement with 10.8±0.02 Å interspacing. Subsequent high-resolution transmission electron microscopy (TEM) studies have indicated an *ABC* stacking sequence (the same as in a fcc arrangement) in these C_{70} films, with the (111) plane parallel to the substrate surface. At room temperature, due to the alignment of the long molecular axes along the $\langle 111 \rangle$ direction, the interspace between adjacent (111) planes deviates from the ideal fcc structure and the C_{70} films can be described as a rhombohedral phase. The occurrence of stacking faults in the *ABC* stacking of (111) planes parallel to the substrate surface has also been observed.[32] The thickness of the C_{70} films used in our experiment was $\sim$1000 Å, as estimated from the attenuation of the substrate core line in XPS. In both EELS and XPS experiments, we have checked that contributions from the substrates were suppressed below the instrumental detection limits and that there was no sign of charging effects. For simplicity, we will thereafter denote the sample as C_{70}(111). All spectra were recorded at room temperature (300 K). In both EELS and XPS experiments, spectra taken 48 h after sample preparation showed no difference from those taken immediately after growth.

III. RESULTS AND DISCUSSION

We first present and discuss the EELS results. A discussion of the XPS C 1*s* satellite structures follows. The excitation cross section of an electronic transition generally depends on the energy of the incident electrons. For this reason, a series of EEL spectra with different incident electron energies (6–100 eV) have been recorded.

Since no detailed calculation of the band structure of C_{70} fullerite exists at present, our tentative assignment of EELS peaks resulting from electronic transitions has essentially been made by reference to the experimental electronic structure obtained by various methods: the valence-band structure probed by ultraviolet photoemission (UPS),[15–17] and the conduction-band structure probed by either inverse photoemission[16] or x-ray absorption spectroscopy.[21]

Figure 1 displays a spectrum recorded with a primary-electron energy of 8.0 eV (resolution 0.04 eV). We note a broad spectral region, extending from 1.1 to 1.45 eV, which is devoid of any feature on a very low background.

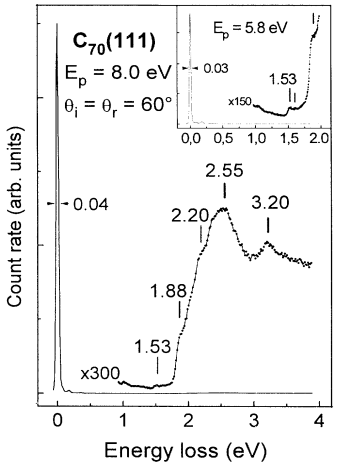

FIG. 1. EELS spectrum of C_{70} fullerite in the near-infrared to visible region. It exhibits the electronic transitions across the energy band gap (the shoulder at 2.20 eV, the pronounced peak at 2.55 eV, and the peak at 3.2 eV) as well as two excitonic levels at 1.53 and 1.88 eV. The spectrum in the inset shows the detail of the feature at 1.53 eV, assigned to the triplet level of a tight-binding Frenkel exciton (see text).

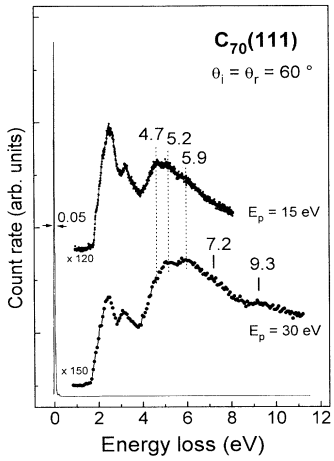

FIG. 2. EELS spectra of C_{70} fullerite taken at two different primary-electron energies (15 and 30 eV). In the visible-ultraviolet region, three features are resolved (marked by dashed lines). From their intensity dependences on the primary-electron energies, the peak at 4.7 eV is ascribed to a π-π^* interband transition of an individual electron; the other two peaks (at 5.2 and 5.9 eV) probably reveal the two split levels of the C_{70} π plasmon. The weak feature at 7.2 eV is interpreted as revealing the first ionization potential of C_{70} fullerite. The feature at $\sim$9.3 eV corresponds to the first π-σ^* transition.

(The feature at $\sim$1 eV results from the overtone of a C_{70} vibrational mode.[33]) Following this featureless region, the first loss feature emerges with an onset at $\sim$1.45 eV and a small but clear peak at 1.53 eV. The inset in Fig. 1 shows a spectrum recorded at lower primary-electron energy (5.8 eV), in which this feature is better resolved and split. This peak at 1.53 eV is, to our knowledge, the lowest electronic excitation in C_{70} fullerite observed so far by any spectroscopy. (A similar peak at slightly higher loss energy, 1.55 eV, has been found by EELS in solid C_{60}.[34] This peak, well below the onset of the optical absorption spectra (AS) of C_{70} in solutions,[3,11] cannot originate from an interband transition across the energy gap in C_{70} fullerite. Note also that there is no discernible structure at a similar energy position in AS of solid C_{70} films.[12] Therefore this 1.53 eV peak must be of excitonic origin. In fact, in highly correlated molecular solids such as C_{60} and C_{70}, the Hubbard U correlation energy [measured to be 1.6±0.2 eV (Ref. 35) and 1.0±0.2 eV (Ref. 29) for the Coulomb repulsion energy between two valence holes on the same site of a C_{60} and C_{70} molecule, respectively] is greater than the typical bandwidth W in these systems. In such systems, the existence of tight-binding Frenkel-type excitons has been theoretically predicted in the energy range 1.5–2 eV.[35] We therefore ascribe the 1.53 eV peak to a Frenkel-type exciton. Such an exciton could be either triplet or singlet, with the triplet at the lowest energy state. Moreover, the excitation probability of the triplet state via exchange processes involving the incident electrons is expected to decrease with increasing incident energy. Therefore our experimental results clearly suggest the triplet character of the excitation at 1.53 eV (see the two spectra in Fig. 1, and the two other spectra in Fig. 2).

Now we discuss the origin of the feature at 1.88 eV. From photoluminescence (PL) spectra of C_{70} in solutions, the singlet-triplet energy splitting had been determined to be about 0.3 eV, as obtained from the two peaks corresponding to vibrational 0-0 transitions.[13] So it seems reasonable to assign the 1.88 eV feature in Fig. 1 to the singlet excitonic level of the aforementioned Frenkel-type exciton. Photoluminescence data of solid C_{70} films reveal three major peaks at 1.82, 1.71, and 1.54 eV,[14] and are thus compatible with our assignment of the relevant EELS features. We note that neither of the two exciton peaks in EELS was resolved as a clear feature in the optical absorption spectra of C_{70} solutions[3,11] or of solid C_{70} films,[12] indicating that they are not dipole-allowed transitions. In EELS, with the participation of the incident electron in the interaction process, excitations other than dipole-allowed transitions can take place. Photoluminescence, on the other hand, measures the deexcitation process regardless of the formation history of its initial state: e.g., it could be an excitonic state decayed from a "normal" excited state via electron-phonon interaction or local lattice deformation following the first excitation process, and so on. Generally, the interpretation of data from a deexcitation spectroscopy (e.g., PL) is more demanding. EELS, being an excitation spectrum, has a certain advantage in this respect. Nevertheless, it is always useful to compare EELS data and PL data in order to get more complete information about the electronic (de)excitation processes in a system.

In Fig. 1, the next loss feature appears at 2.20 eV, above the onset of the optical absorption spectra of C_{70} in solutions[3,11] or of solid C_{70} films.[12] We tentatively assign it to the first electronic transition across the band gap in C_{70} fullerite (i.e., the solid-phase analogue of the

HOMO-LUMO transition in the C_{70} molecule). Normally, the HOMO-LUMO transition in a C_{70} molecule should be dipole forbidden. But calculations have demonstrated the bunching of different molecular levels in C_{70}, including those in proximity of the HOMO and the LUMO.[23,24] So it is likely that C_{70} molecular orbitals with different parities are intermixing significantly to form energy bands in C_{70} fullerite. Another possibility is that, upon interaction with the incident electron beam, the local crystalline symmetry is slightly perturbed and so are the molecular orbitals from which the energy bands derive. In both cases, the direct consequence is that the usual dipole selection rule no longer strictly applies and some optically forbidden transitions take place. We should note that due to the correlation effects the onset of the interband transition measured in EELS does not provide directly the fundamental energy gap of C_{70} fullerite in its ground state.

In the EEL spectrum presented in Fig. 1, an outstanding peak emerges at 2.55 eV loss energy: it clearly corresponds to the AS band centered at 468 nm (2.64 eV) for C_{70} in solutions[3,11] or to the AS band centered at 2.4–2.5 eV for solid C_{70} film,[12] considering the similarity in their peak positions and line shapes. It constitutes the first (group of) dipole-allowed electronic transition(s) in C_{70} fullerite.

Another common way to measure the energy separation between an occupied and an unoccupied electronic state is by means of direct and inverse photoemission spectroscopy (PES-IPES), where one electron is either photoemitted from the occupied state or added to the empty state through a radiative process. It is clear that all possible optical transitions across the gap could, at least in principle, be correlated with some transition processes from an occupied band state (probed by PES) to an unoccupied band state (probed by IPES). Theoretical calculations of the C_{70} molecular orbitals reveal a significant bunching of the energy levels near the gap.[23,24] Therefore we can reasonably suppose that in C_{70} fullerite the energy states with even and odd angular symmetries tend to distribute homogeneously in the first occupied (and unoccupied) energy band near the gap. By neglecting the matrix-element effect, it can be readily shown that the average distance between the first occupied and unoccupied bands ought to coincide with the main energy-loss peak in EELS if there were no electron-electron correlation effects in the system under investigation.

However, from the PES-IPES measurement, an average separation of 3.7 ± 0.2 eV was found for the highest occupied band to the lowest unoccupied band in C_{70} fullerite,[16,17] corresponding to the $(N\pm1)$-electron system. This energy separation (3.7 ± 0.2 eV) is considerably greater than the corresponding value (2.55 eV) measured by EELS, again due to the fact that the correlation effect is important in C_{70} fullerite. In fact, comparing these two transition energies measured respectively by EELS and PES-IPES gives a direct measure of the Hubbard correlation energy ($U\approx1.2\pm0.2$ eV) for charged particles on the same molecule. Indeed, for a molecular solid like C_{70} fullerite, the individual molecule wave functions are only weakly delocalized. Consequently, the interband electron transitions, particularly those between the energy bands near the energy gap, should retain their largely localized character. Therefore the energy to separate an electron-hole pair on the same site (as in the case of EELS) to infinity (as in the case of PES-IPES) is appreciable and it constitutes the main contribution to the Hubbard correlation energy. For C_{60} fullerite, from an analogous comparison of the EELS (Ref. 34) and PES-IPES (Refs. 16,17) results, the Hubbard correlation energy can be determined to be (1.5 ± 0.2 eV). We note that the ratio of the Hubbard correlation energies corresponding to C_{60} and C_{70} fullerites is consistent with the ratio of the short to long molecule axes to which the Coulomb interactions should be roughly inversely proportional, thus reflecting mainly the geometrical difference between these fullerene molecules.

Local hole-hole repulsive energy in a system provides an alternative measure of this correlation effect.[35] From the difference of the two hole binding energies of the carbon Auger KVV line with respect to the self-convolution of the valence band probed by ultraviolet photoemission spectroscopy (UPS), this local hole-hole repulsion had been measured to be 1.6 ± 0.2 eV in C_{60} fullerite[35] and 1.0 ± 0.2 eV in C_{70} fullerite.[29] We see that these values are essentially the same as those obtained by comparing the EELS and PES-IPES data, just as can be expected from the common p_π orbital character of the bands near the energy gap of C_{70} (or C_{60}) fullerite.

The EELS spectra in the visible-ultraviolet region show several further peaks or shoulders up to 12 eV. In Fig. 2, we show two spectra taken with primary-electron energies of 15 and 30 eV. The peak at 3.2 eV is another dipole-allowed transition across the energy gap; it correlates with the sharp AS peak at 378 nm (3.28 eV).[3,11] We note that the energy separation between this peak and the prominent peak at 2.55 eV corresponds to the energy separation between the first and second empty bands of C_{70} fullerite as measured by both inverse photoemission[16,17] and x-ray absorption spectroscopy.[21] Accordingly, we assign the peak at 3.2 eV as revealing the transition from the highest occupied band to the second lowest unoccupied band envelope in C_{70} fullerite.

Further above in loss energy, the next group of peaks, culminating at ~6 eV, is composed of at least three distinct features: the first one at ~4.7 eV with roughly constant intensity when the primary-electron energy increases from 15 to 30 eV, indicating its impact scattering nature; and two other peaks, the intensities of which increase significantly with the primary-electron energy, pointing to a long-range dipole scattering. Following the argument developed by Lucas *et al.*[34] on the differentiation of the loss peak natures from their intensity variation with incident electron energies in EELS, we conclude that the peak at 4.7 eV stems from interband transitions of an individual electron; whereas the two peaks at 5.2 and 5.9 eV result from collective excitations. The feature at ~4.7 eV is assigned to the interband transitions of an individual electron, probably from the HOMO-derived band to the third lowest-lying empty

band or from the states in the second highest valence-band envelope (in UPS) to the second lowest empty band (in PES).

We interpret the two latter peaks as revealing the two split levels of the π plasmon of C_{70}. This π-plasmon level splitting of C_{70} is a direct consequence of its ellipsoidal molecular shape: the collective dipolar excitation of the π electrons along the long molecular axis has different resonance frequency from that along the short axes. Previously, from the EELS of free C_{70} clusters, a detailed intensity analysis of the peak components in the π-plasmon energy range as a function of incident electron energies strongly suggested its double splitting character: two components, also at loss energies of 5.2 and 5.9 eV, have been shown to increase in intensity with incident electron energies while keeping their intensity ratio constant.[19,36] Therefore they have been ascribed to the two split levels of the π plasmon of the C_{70} molecule.

In a theoretical investigation of the van der Waals cohesion and plasmon excitations in fullerenes, Lambin and Lucas introduced a simple model of C_{60} (or C_{70}) molecules by treating them as spherical (or elliptical) shells of isotropic dielectric continuum. By employing classical electrostatics to calculate the polarizabilities of the modeled C_{60} and C_{70}, the general expression of the molecular-axis-dependent plasmon modes was derived as a function of their dielectric constants and geometric parameters. Based on this, the optical ultraviolet absorption cross sections of C_{60} and C_{70} were computed.[28] Later, by using the same theoretical approach and a similar model of the fullerene molecules, Ding found that the ratio of the plasmon energies along the long and short molecular axes was 1:1.12,[36] in good agreement with the experimental value of 1:1.13 (i.e., 5.2:5.9). Therefore this simple model provides a satisfactory explanation of the double splitting of the π-plasmon level in gas-phase and solid C_{70}. In EELS on C_{70} fullerite (see Figs. 2 and 3), at higher incident energy where the 4.7 eV peak resulting from a π-π^* transition has little influence on the peak

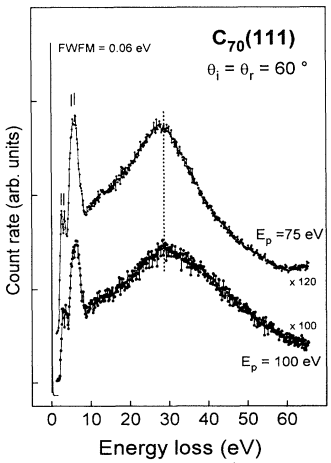

FIG. 3. EELS spectra of C_{70} fullerite taken at primary-electron energies of 75 and 100 eV. The broad hump culminating at $\sim$28 eV results from the $(\sigma+\pi)$-plasmon excitation, the collective excitation of all valence electrons of C_{70}.

shape of the π plasmon, the peak at 5.9 eV is invariably stronger than the 5.2-eV peak. This can also be explained by the above model in which the peak at 5.9 eV represents the plasmon excitation along two short axes, while the peak at 5.2 eV corresponds to the excitation mode along the unique long axis of a C_{70} molecule, further noting that at room temperature the free rotation of the molecule will statistically favor the short-axis excitations. Our observation of the π-plasmon level splitting in C_{70} fullerite confirms that C_{70} in the solid phase retains to a large extent the molecular properties, as far as the collective excitations of the π valence electrons are concerned.

Two weak features at 7.2 and 9.3 eV are visible in the spectrum recorded with a primary energy of 30 eV (Fig. 2). We assign the weak feature at 7.2 eV to the first ionization potential (IP) of C_{70} fullerite. This IP value is in agreement with the result of the ultraviolet photoemission measurement on solid C_{70} which locates the first ionization band at about 7.4 eV below the vacuum level.[15] The feature at 9.3 eV could be explained by the electronic transition from the highest occupied band into the lowest-lying σ^* band in C_{70} fullerite.

In Fig. 3, we present two spectra recorded at the primary-electron energy of 75 and 100 eV, respectively. The broad hump culminating at $\sim$28 eV correlates with the $(\sigma+\pi)$ plasmon, the collective excitation of all valence electrons of the C_{70} molecule. Its broadness precludes any observation of possible plasmon level splitting, in contrast to the case of the π plasmon.

This $(\sigma+\pi)$ plasmon has been detected in gas-phase C_{70} and in solid C_{70}.[18–20] The measured $(\sigma+\pi)$ plasmon energy is invariably higher in the solid phase than in the gas phase. This can be understood as follows. Generally, for the gas phase the plasmon energy can be directly determined by the polarizability of the molecule $\alpha(\omega)$; for the solid phase, it is determined by the dielectric response $\epsilon(\omega)$. The two quantities, $\alpha(\omega)$ and $\epsilon(\omega)$, are related by the Clausius-Mossotti equation[37] which accounts for the solid-state effect of extramolecular screening on the polarization property of the solid material. In the case of C_{60} and C_{70}, it can easily be derived from the Clausius-Mossotti equation that the $(\sigma+\pi)$ plasmon energy is several eV higher in the solid phase than in the gas phase.[20,36] In a more refined theory,[38] the excitation of multipole modes in solid fullerene has also been invoked to explain the displacement of the plasmon peak of fullerites towards higher energy. Note also that background removals with the view of eliminating multiple-scattering contributions could move the $(\sigma+\pi)$ plasmon peak to lower energy by 1–2 eV.[20]

As pointed out elsewhere,[28,38] the relatively big size of the fullerene molecules makes the contribution from the excitation of the multipole plasmon modes important. Moreover, the interaction between the π and σ electrons and the resultant complex character of the bondings (basically sp^2 hybridization with a small sp^3 component[23]) in fullerenes should also be taken into consideration in order to explain the detailed behavior of the $(\sigma+\pi)$ plasmon. A simple free-electron-like model is not adequate for this

purpose.

We now turn to the XPS C 1*s* satellite structures (see Fig. 4). The C 1*s* line, at 285.0 eV binding energy relative to the Fermi level of the grounded spectrometer, has a full width at half maximum (FWHM) of 0.75 eV. This is 0.10 eV broader than the C 1*s* line of a C_{60} film of comparable quality, reflecting five inequivalent carbon sites in the ellipsoidal structure of C_{70} molecule.

The first peak at 2.5 eV from the C 1*s* main line could probably be partly explained by the electronic transition between highest occupied and lowest unoccupied bands in the ionized species C_{70}^{+}. It is likely that some contribution also comes from the (off-site) inelastic scattering process, taking into account the similarity in line shape between this peak and the EELS peak at 2.55 eV (see Fig. 1). Indeed, this shakeup structure at 2.5 eV shows a clear asymmetry with a shoulder on the higher-binding-energy side, pointing to a feature at ~3.2 eV. This observation is consistent with the EELS result where a distinct peak emerges at 3.2 eV loss energy. Due to effects such as the electron correlation and the interaction of the valence hole and the electron excited to the lowest unoccupied band with the core hole, the observed value does not correspond directly to the ground-state energy separation between the highest occupied and lowest unoccupied bands of C_{70} fullerite.

The next group of peaks, extending from 4.5 to 6.5 eV, culminates at 6.0 eV with a pronounced shoulder at ~4.7 eV. In analogy to EELS, we interpret the feature at ~4.7 eV as revealing the interband transitions of an individual electron, probably from the HOMO-derived band to the third lowest-lying empty band (in IPES) or from the states in the second highest occupied band (in UPS) to the second lowest empty band (in IPES). As already discussed, the excitation of the π plasmon of C_{70} gives rise to the features at 5–6 eV. Here the splitting of the π-plasmon levels was not resolved, probably due to the instrumental resolution limit. Moreover, the intermixing character of the two sorts of loss mechanism, i.e., the on-site contribution coming from the excited states of the ionized molecule from which the photoelectron is ejected, and the off-site contribution from the inelastic scattering that the photoelectron experiences when it propagates through the lattice, could also have some smearing effect.

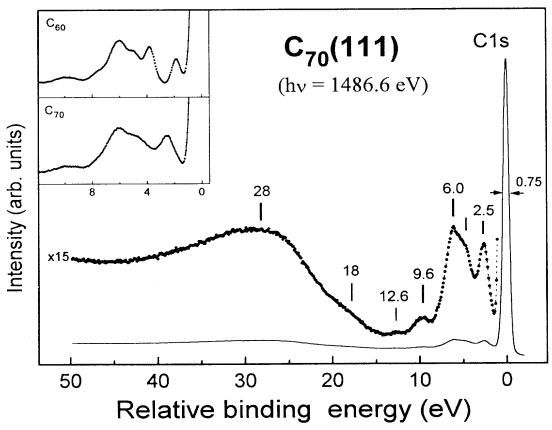

FIG. 4. XPS C 1*s* line satellite structures of C_{70} fullerite. The first shakeup peak, at 2.5 eV from the main line, reveals the center-to-center electron transition from the highest occupied band to the lowest unoccupied band. The peak at ~6 eV correlates with the excitation of the C_{70} π plasmon; the broad hump at ~28 eV corresponds to the $(\sigma+\pi)$ plasmon. The feature at 9.6 eV reflects the onset of the π-σ^* transitions. The inset shows the shakeup structures of C_{60} and C_{70} near their respective C 1*s* core lines. Energies are references to C 1*s* lines. (The upper panel of the inset is reproduced from Ref. 39.)

Three more features, respectively at 9.6, 12.5, and ~18 eV, were detected. In analogy to EELS, we assign the peak at 9.6 eV to the electronic transition from the highest occupied band into the lowest-lying σ^* band. At this point, it is instructive to note that for both C_{60} and C_{70} fullerites, in XPS C 1*s* satellite structures, there is a peak at almost identical position (~9.6 eV) from their C 1*s* lines (see Ref. 17, and Fig. 4 of this paper). Previously, the XAS study on solid C_{60} and C_{70} had already shown that their respective energy separation between the LUMO-derived band and the lowest-lying σ^* band is almost the same.[21] All this indicates one fact: for solid C_{60} and C_{70}, differences in their molecular shape and number of valence electrons per molecule play only a minor role in the distribution of their leading σ^* states, in contrast to those electronic states closer to the Fermi level where important differences have been observed between the two fullerites.[16,17] Indeed, it can be concluded that the width of their respective π^* bands is almost the same for C_{60} and C_{70}. However, probably due to the different cross sections of electrons with different energies to excite the π-σ^* transitions, the peaks corresponding to the first π-σ^* transition in our EELS and XPS satellite data appear at slightly different positions (~9.3 eV in EELS and ~9.6 eV in the XPS satellite structures).

The weak feature at 12.5 eV could be explained by a further π-σ^* transition, probably from the third highest valence band in UPS (2.7–3.3 eV from the highest occupied band, thus in agreement with the observed energy separation of the corresponding features in EELS) to the lowest σ^* band. In fact, both from the energy level calculation of the C_{70} molecule[23] and the experimental data obtained by UPS on C_{70} fullerite,[15–17] the third valence-band envelope of C_{70} fullerite (or in the corresponding energy range of the C_{70} molecule) had been found to have a high density of states. Regarding the feature at ~18 eV, it could be caused by the excitation of certain σ-σ^* interband transitions, which are expected to be strong at this energy range.[18]

In the inset of Fig. 4, we present the XPS shakeup structures of C_{60} and C_{70} fullerites within 12 eV from their respective C 1*s* main lines. These spectra have been recorded from C_{60} and C_{70} films of similar quality. Our high-resolution data are in good overall agreement with the recently published results.[17]

IV. CONCLUSIONS

The combined study of highly ordered C_{70} films by EELS and XPS C 1*s* satellite structures has provided a comprehensive picture of the electronic transitions and excitations of the system. In particular, two excitonic

levels (1.53 and 1.88 eV), interpreted as the triplet and the singlet of a tight-binding Frenkel exciton resulting from the residual electron-hole Coulomb attraction in the system, were observed. The first interband electron transitions (solid-phase analogue of the HOMO-LUMO transition) corresponds to a feature at ~ 2.20 eV. Other major individual transitions across the energy gap and the collective excitations of the valence electrons were also identified. The splitting of the π-plasmon levels of C_{70} fullerite (induced by the ellipsoidal molecular shape) was observed, confirming that the molecular character is to a large extent retained in C_{70} fullerite. By comparing the corresponding features in EELS and PES-IPES (direct and inverse photoemission) data, the Hubbard U correlation energy was determined to be (1.2 ± 0.2 eV). Finally, our experimental results confirm the earlier XAS results suggesting that the C_{70} and C_{60} fullerites have nearly the same π^* bandwidth and that their leading σ^* states have similar structures.

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